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BEYER WEAVER & THOMAS, LLP

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500 12th Street, Suite 200, Oakland, CA 94607
Telephone: (510) 663-1100 Facsimile: (510) 663-0920
www.beyerlaw.com

FACSIMILE COVER SHEET

July 18, 2006

Receiver: Examiner Jarrett J. Stark
(USPTO Central Fax)

FAX #: (571) 273-8300

Sender: Denise S. Bergin
Our Ref. No.: NOVLP082/NVLS-2893

Application No: 10/772,109

Re: 1. Communication
2. Article 1: A definition of metallocene from the "Encyclopedia of Chemistry"
3. Article 2: "Metallocene" entry from Wikipedia

Pages Including Cover Sheet(s): 07

cc: Examiner Jarrett J. Stark
(571) 273-6005

MESSAGE:**CONFIDENTIALITY NOTE**

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JUL 18 2006

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Dalton et al.

Attorney Docket No.:
NOVLP082/NVLS-0002893

Application No.: 10/772,109

Examiner: Jarrett Stark

Filed: February 3, 2004

Group: 2823

Title: USE OF METALLOCENES TO INHIBIT
COPPER OXIDATION DURING
SEMICONDUCTOR PROCESSING

CERTIFICATE OF FACSIMILE TRANSMISSION
I hereby certify that this correspondence is being transmitted
by facsimile to fax number 571-273-8300 to the U.S. Patent
and Trademark Office on July 18, 2006.

Signed:

Tara Hayden

COMMUNICATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Per Tara Hayden's conversation with Examiner Jarrett Stark on July 18, 2006, please find attached the two articles, the "Metallocene" entries from the "Encyclopedia of Chemistry" and from Wikipedia, for the above referenced matter. The applicant filed a response to the Final Office Action dated May 5, 2006 on July 7, 2006 and these papers were unintentionally not attached. Please file these documents in the subject application with the July 7, 2006 response.

The Commissioner is authorized to charge any additional fees that may be due to our Deposit Account No. 500388 (Order No. NOVLP082).

Respectfully submitted,
BEYER WEAVER & THOMAS, LLP

Denise Bergin
Denise S. Bergin
Reg. No. 50,581

P.O. Box 70250
Oakland, CA 94612-0250
510-663-1100

VAN NOSTRAND'S

ENCYCLOPEDIA OF CHEMISTRY

Fifth Edition

Edited by

Glenn D. Considine



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1. Chemistry—Encyclopedias. I. Considine, Glenn D. II. Van Nostrand Reinhold
encyclopedia of chemistry.

QD4.V36 2005
540'.3—dc22

EPA PRETREATMENT STANDARDS FOR AQUEOUS DIS-

| mg/L | Existing sources, PSSE ^c | | New source, PSNS ^c | |
|------------------------|-------------------------------------|---------|-------------------------------|---------|
| | 1 Day | 30 Days | 1 Day | 30 Days |
| total | 0.69 | 0.26 | 0.11 | 0.07 |
| | 2.77 | 1.71 | 2.77 | 1.71 |
| | 3.38 | 2.07 | 3.38 | 2.07 |
| | 0.69 | 0.43 | 0.69 | 0.43 |
| | 3.98 | 2.38 | 3.98 | 2.38 |
| | 0.43 | 0.24 | 0.43 | 0.24 |
| | 2.61 | 1.48 | 2.61 | 1.48 |
| | 1.2 | 0.65 | 1.2 | 0.65 |
| | 0.86 | 0.32 | 0.86 | 0.32 |
| total organic organics | 2.13 | 2.13 | | |

Manufacturers performing metal finishing, including electroplating, discharge PWs.
6-10.
value. PSSE = pretreatment standards for existing sources; PSNS = standards for new sources.

Donnan dialysis, electrodialysis, electrowinning, evaporation, flocculation, hydrolysis, incineration, ion exchange, metallic treatment, neutralization, oxidation, pH adjustment, photolysis, precipitation, process modification, reduction, reverse osmosis, salt splitting, sedimentation, solidification, and spray rinsing.

GERALD A. KRULIK
Applied Electroless Concepts, Inc.

NENAD V. MANDICH
HRM Engineering Company

Additional Reading

J. J. ed.: *Electroplating Engineering Handbook*, 4th Edition, Van Nostrand Reinhold Co., Inc., New York, NY, 1984.
Finishing Guidebook and Directory, Vol. 92, No. 1A, Elsevier Publishing, New York, 1984; collected vols., Publications, Inc., Hackensack, NJ, updated yearly.
Surface Finishing, Semiconductor International, and *Metal Finishing* provide some of the best information on innovative metallizing methods.

W. H. *The Properties of Electrodeposited Metals and Alloys*, 2nd Edition, American Electroplaters and Surface Finishers Society, Orlando, FL, 1986.

METALLOBIOMOLECULES. Natural products, the biologically active forms of which contain one or more metallic elements. Metalloproteins may be transport and storage proteins, such as ferrim (Fe), ferritin (Fe), transferrin (Fe), ceruloplasmin (Cu), albumin (Fe), or hemoglobin (Fe); or they may be enzymes, such as peptidases (Zn), aminopeptidases (Mg, Mn), phosphatases (Mg, Ca), hydroxylases (Fe, Cu, Mo), or isomerases and synthetases, such as enzymes (Co). Metallobiomolecules also may be nonproteins, such as apophyses (Fe) or chlorophyll (Mg). Ibers and Holm provide an excellent review of metallobiomolecules in *Science*, 209, 223-235 (1980).

METALLOCENES. A class of neutral transition metal compounds containing two cyclopentadienyl (C_5H_5) ligands π -bonded to a central metal atom in a "sandwich" structure, as exemplified by ferrocene below.

The original metallocene, ferrocene, was first reported simultaneously and independently by two groups of workers in 1951. Müller, Tebbe, and Hahn at British Oxygen Ltd. passed cyclopentadienes over iron powder and ammonia catalyst; Kealy and Pauson at Duquesne University treated iron chloride with cyclopentadienyl magnesium bromide. Both groups obtained the same orange, air-stable, hydrocarbon-soluble crystals (m.p. 199°C) and proposed a sigma bonded structure for this first organometallic compound of iron. Within a year groups at Harvard University including Wilcock, Wilkinson, Rosenblatt and Whiting revealed that $C_{10}H_{10}Fe$ has unusual thermal stability, has no dipole moment, and undergoes typical aromatic substitution reactions; whereupon, they proposed the novel sandwich structure and advanced the name *ferrocene* to reflect both the iron content of the material and its aromaticity. X-ray crystallographic studies

vapor phase the barrier to rotation of the rings has been shown to be very small.

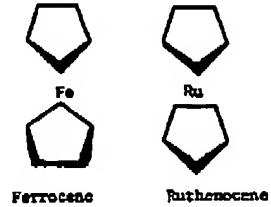
One proposed bonding scheme, using a molecular orbital model, calls for utilizing the π orbitals of the C_5H_5 group and the $d_{xx}, d_{yy}, d_{zz}, p_x, p_y$, and p_z iron orbitals to obtain a total of six bonding orbitals with the twelve π -electrons from the rings to fill them.

After the discovery of ferrocene many additional metallocenes and their derivatives were prepared, including titanocene (green), vanadocene (purple), chromocene (scarlet), cobaltocene (purple-black) and nickelocene (green). Dicyclopentadienyl manganese (amber) is ionic, and dicyclopentadienyl mercury, tin and lead are sigma bonded; their derivatives are not properly called metallocenes. In the second and third transition series, only ruthenocene and osmocene are known as simple, neutral metallocenes; the other metallocenes are known as cations (e.g. Cp_2Ti^+) or with additional ligands such as halide or hydride attached to the metal atom, as in Cp_2TiCl_2 , Cp_2ReH , Cp_2TaH_3 , etc. Though several preparative approaches are known, the most general reaction leading to metallocenes is the treatment of a metal halide with sodium cyclopentadienide in tetrahydrofuran. Ideally a +2 salt of the metal is used, although excess of the cyclopentadienide will often reduce a higher valent metal halide to a lower oxidation state during the reaction.

Chemically, ferrocene undergoes many typical aromatic substitution reactions such as Friedel-Crafts acylation or alkylation, sulfonation, mercuration, lithiation, the Vilsmeier reaction and the Mannich reaction (with dimethylamine, formaldehyde and acetic acid). Its reactivity is very great ("superaromatic") and is comparable in rate to that of phenol. Mono- and disubstitution on one or both rings can be realized, though some measure of control to predominantly mono- or disubstitution can be exercised by adjusting conditions.

However, the central metal atom in ferrocene imposes some limitations on the chemistry of the system or provides in some cases additional reaction pathways. For example, the central iron atom is readily and reversibly oxidized from the Fe(II) state to Fe(III) in the form of the water-soluble red-blue dichroic ferrocinium ion. This oxidation occurs with halogens or with nitric acid so that direct aromatic halogenation and nitration cannot be realized; however, halo- and nitroferrocene have been prepared by indirect methods. Aminoferrocene cannot be diazorized, presumably due to oxidative destruction of the system. Coupling with diazonium salts is anomalous; ferrocene reduces diazonium salts to phenyl radicals in aqueous or nonaqueous solution to yield Gomberg (phenylation) products. Condensation with aldehydes in acid solution gives rearranged products due to a role that the iron atom can play. The central iron atom is readily protonated in strong acid media.

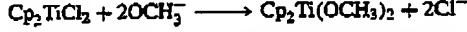
In the solid state ruthenocene and osmocene prefer the eclipsed, pentagonal prismatic structure and in solution exhibit a chemistry similar to that of ferrocene. The other metallocenes, on the other hand, are quite different chemically, none of them showing the typical aromatic substitution reactions of ferrocene.



Cobaltocene is rapidly oxidized in air or in solution (it liberates H_2 from water, slowly) to yield the very stable yellow +1 cation, which has been reported to be stable to aqua regia. Neutral cobaltocene reacts with alkyl and acyl halides to give adducts $(C_5H_5)(C_5H_5R)Co^+X^-$ in which the substituted ring is π -bonded to the cobalt as a diene.

Nickelocene, on the other hand, is more slowly oxidized and undergoes addition of suitable activated olefins to one ring converting it to a bicyclic ligand. Some ligand replacement reactions are also known for nickelocene.

Titanocene derivatives undergo substitution reactions at the metal atom:



Metallocene

From Wikipedia, the free encyclopedia

In chemistry, and in particular, in organometallic chemistry, a metallocene is a compound with the general formula $(C_5R_5)_2M$ consisting of two cyclopentadienyl anions (Cp) bound to a metal center in the oxidation state II.

Contents

- 1 Definition
- 2 Features of metallocenes
- 3 Derivatives
- 4 References

Definition

The general name metallocene is derived from ferrocene, systematically *bis(η^5 -cyclopentadienyl)iron*. According to the definition by IUPAC, a metallocene contains a transition metal and two cyclopentadienyl ligands coordinated in a *sandwich structure*, i. e. the two cyclopentadienyl anions are co-planar with equal bond lengths and strengths. The nature of the bonding of the organic ligand to the metal is referred to as its "hapticity" and is indicated by the Greek letter eta (η). The equivalent bonding of all 5 carbon atoms of each cyclopentadienyl ring is denoted as η^5 , pronounced "pentahapto".

Features of metallocenes

A notable feature of all metallocenes is their high thermal stability (up to and over 500°C). All neutral metallocenes are soluble in common organic solvents and can be purified by vacuum sublimation. Metallocenes of all 3d-row elements are known, but with the exception of ferrocene all of these are sensitive to air, paramagnetic and do not possess a closed-shell electron structure (see 18-Electron rule).

X-ray diffraction studies have shown that the cyclopentadienyl rings might be either eclipsed or staggered. For non-substituted metallocenes the energy difference between the staggered and eclipsed conformations is only 8 kJ/mol. Ferrocene and osmocene take on an eclipsed conformation at low temperatures, while pentamethylcyclopentadienyl ligands are always in a staggered conformation to minimize steric hindrance between the methyl groups.

In contrast to the more strict definition proposed by IUPAC, which requires a d-block metal and a sandwich structure, the term metallocene and thus the denotation -ocene, is applied in the chemical literature also to non-transition metal compounds, such as Cp_2Ba , or structures where the aromatic rings are not co-planar, such as found in manganocene or titanocene dichloride, Cp_2TiCl_2 .

Derivatives

Derivatives of metallocenes include structures with an intramolecular bridge between the two cyclopentadienyl rings (ansa-metallocenes), compounds with just one facially-bound planar organic ligand (half-sandwich compounds), compounds with three Cp anions and two metal cations in alternating order (tripledecker

configuration) and compounds where one cyclopentadienyl ligand is replaced by three other ligands (piano stool configuration).

References

A. Salzer, NOMENCLATURE OF ORGANOMETALLIC COMPOUNDS OF THE TRANSITION ELEMENTS (IUPAC Recommendations 1999) (http://www.iupac.org/publications/pac/1999/71_08_pdf/7108salzer_1557.pdf)

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Category: Metallocenes

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